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(54) DIRECT CONTACT TYPE METHANOL FUEL CELL

(57)Abstract:
PROBLEM TO BE SOLVED: To prevent the lowering of output due to the crossover of methanol of a negative electrode with a positive electrode, and provide stabilized high output for a long time by using a catalyst, which selectively and electrochemically reduce oxygen, for positive electrode, and using a catalyst, which electrochemically oxidizes methanol, for negative electrode.
SOLUTION: A positive electrode is provided with a catalyst formed of carbon carrying gold and silver, which selectively and electrochemically reduce oxygen, or an alloy having at least one of gold and silver, or the mixture thereof, and a negative electrode is provided with a catalyst, which electrochemically oxidizes methanol, so as to form a direct contact type methanol fuel cell. With this structure, even in the case where a crossover that methanol as a fuel of the negative electrode is moved to the positive electrode as an opposite electrode through the electrolyte is generated, since the catalyst of the positive electrode is inert to methanol for electrochemical oxidization, the only electrochemical reduction of oxygen is performed, and electrochemical oxidization of methanol is not performed. Lowering of output due to the crossover is thereby prevented.

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CLAIMS

[Claim(s)]
[Claim 1] The direct mold methanol fuel cell characterized by coming to have the positive electrode which has the catalyst which carries out electrochemical reduction of the oxygen selectively, and the negative electrode which has the catalyst which carries out electrochemical oxidation of the methanol.
[Claim 2] The direct mold methanol fuel cell according to claim 1 characterized by being these [the carbon with which the catalyst of a positive electrode supported the alloy which has either / at least / the carbon which supported gold or silver, gold or silver, or] one sorts, or two sorts or more of mixture.
[Claim 3] The direct mold methanol fuel cell according to claim 1 characterized by the catalysts of a positive electrode being these [which have either / at least / a gold dust object, silver fine particles, carbon fine particles, gold or silver / these / the alloy-powder object or] one sorts, or two sorts or more of mixture.
[Claim 4] The direct mold methanol fuel cell according to claim 1, 2, or 3 characterized by an electrolyte being a solid-state poly membrane.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates the methanol which is a fuel with a negative electrode to the direct mold methanol fuel cell which oxidizes directly and electrochemically.
[0002]
[Description of the Prior Art] The fuel cell (FC) carried in current and an electric vehicle has the polymer electrolyte fuel cell (PEFC) in use which uses a solid-state poly membrane for an electrolyte, and the most uses pure hydrogen for a fuel. However, although pure hydrogen is stored with a bomb or a hydrogen storing metal alloy, considering the tooth space and load limits when in the car was restricted, there is a problem in utilization. Then, an energy density is high also weight-wise and in volume, and that handling also uses an easy methanol as a fuel has attracted attention.
[0003] In order to use this methanol as a fuel, there are an indirect mold to which send into a fuel cell and an electrochemistry target is made to react after reforming a methanol in hydrogen, and a direct mold which the methanol of a liquid is sent [mold] into a fuel cell as it is, and makes it react to an electrochemistry target. Since a direct mold can simplify equipment compared with an indirect mold, it is suitable as a fuel cell for electric vehicle loading.
[0004] A direct mold methanol fuel cell consists of a positive electrode, a negative electrode, and an electrolyte inserted among them. There are a thing using the alkaline electrolytic solutions, such as what uses the acid electrolytic solutions, such as a sulfuric-acid water solution, and a potassium hydroxide, and a thing using a solid-state poly membrane in an electrolyte further. As a catalyst of a positive electrode, the carbon fine particles which supported Pt are a catalyst of a negative electrode. The carbon fine particles which supported Pt or Pt-Ru are used.
[0005] In a direct mold methanol fuel cell, oxygen reduction in air is performed by the positive electrode, and oxidation of the methanol of a liquid is electrochemically performed by the negative electrode. The reaction formula is shown below.
positive-electrode: -- 3/2O2+6H++6e-->3H2O negative-electrode: -- CH3 OH+H2 -- O->CO2+6H++6e- total reaction: -- CH3OH+3/2O2+H2O->CO2+3H2O -- [Problem(s) to be Solved by the Invention] However, it has the problem that this direct mold fuel cell has the low output of a cell. It originates in the so-called crossover which the methanol of a negative electrode moves to the positive electrode which is a counter electrode through an electrolyte. It is a kind of chemical short circuit intrinsically, the electrochemical oxidation of a methanol arises in electrochemistry reduction and coincidence of oxygen with a positive electrode, and the crossover of the methanol which is a fuel reduces an output remarkably. This is because the catalyst used for the positive electrode of the conventional direct mold methanol fuel cell is activity also in the electrochemical oxidation of a methanol at the electrochemical reduction and coincidence of oxygen (M. 156 P.Hogrth, a platinum metals review, 40 (4), 1996). However, about a concrete configuration, reference is not made at all.
[0006]
[Means for Solving the Problem] this invention person then, by considering as the direct mold methanol fuel cell equipped with the negative electrode which has the catalyst which carries out electrochemical oxidation of the methanol for the catalyst which carries out electrochemical reduction of the oxygen to a positive electrode selectively by inquiring wholeheartedly to a negative electrode The carbon which supported the alloy which has either [at least] the carbon which made it possible to prevent decline in the output by crossover, and effectiveness, and supported gold or silver further, gold or silver, Or a gold dust object, silver fine particles, carbon fine particles or gold, the alloy-powder object that has at least silver one side, Or for

the electrochemical reduction of oxygen, to being activity, since these one sorts or two sorts or more of mixture was inactive, it found out that it was suitable as a catalyst of the positive electrode of the direct mold fuel cell of this invention at the electrochemical oxidation of a methanol.
[0007]
[Embodiment of the Invention] Even if the crossover which the methanol which is the fuel of a negative electrode by considering as a direct mold methanol fuel cell equipped with the catalyst which carries out electrochemical oxidation of the methanol for the catalyst which carries out electrochemical reduction of the oxygen to a positive electrode selectively to a negative electrode moves to the positive electrode which is a counter electrode through an electrolyte arises, since the catalyst of a positive electrode is inactive at the electrochemical oxidation of a methanol, only electrochemical reduction of oxygen is performed and electrochemical oxidation of a methanol is not performed. Therefore, lowering of the output by crossover does not arise.
[0008] In addition, "the catalyst which carries out electrochemical reduction of the oxygen selectively" in this invention means the following 1 or 2. 1: The catalyst to which only oxygen is returned electrochemically. 2: The catalyst whose amount of electrochemical reduction of oxygen is a minute amount very much compared with the amount of electrochemical oxidation of a methanol although the electrochemical oxidation of a methanol is also produced in the electrochemical reduction and coincidence of oxygen.
[0009] Moreover, the shape of fibrous, a globular shape, and a flake etc. may be raised, and the carbon in this invention may be fine particles, and may be a sintered compact etc., and it is not restricted to these, either.
[0010]
[Example] Hereafter, a suitable example explains this invention.
[0011] As an electrolyte, the solid-state poly membrane (the Du Pont make, the perfluoro sulfonic acid film and Nafion-117) was chosen. a catalyst electrode-zygote used as the negative electrode the porous carbon paper which applied the catalyst mixture of the carbon catalyst and the PTFE powder which used as the positive electrode the porous carbon paper which applied catalyst mixture with the solution (the Aldrich make, Nafion solution) which consists of the same presentation as the carbon catalyst and the PTFE fine particles which supported gold, and a solid-state poly membrane, and supported platinum, and it boiled and carried out the hotpress to both sides of a solid-state poly membrane, and it created it in them. Here, acetylene black was used for carbon.
[0012] Thus, the fuel cell was constructed using the obtained catalyst electrode-zygote, and delivery and its property with the passage of time were investigated [air] for the methanol to the positive electrode at the negative electrode. The property with the passage of time was investigated on conditions with the same said of the conventional fuel cell which used as the positive electrode the porous carbon paper which applied catalyst mixture with the solution which consists of the presentation same as a comparison as the carbon catalyst and PTFE fine particles which supported platinum, and a solid-state poly membrane.
[0013] In drawing 1 , A is the cell property of the example concerning this invention, and B is the conventional cell property.
[0014] Here, a test condition is shown below.
[0015] discharge current: -- 200mA[/cm] 2 positive-electrode supply: -- the terminal voltage of a conventional-type methanol fuel cell is falling with time by crossover of the positive electrode of the methanol of a negative electrode from air, a 5kg/cm2G negative-electrode:methanol 50vol.% water solution, and ordinary pressure operating temperature:80-degree-C drawing 1. This is because the carbon catalyst which supported the platinum of a positive electrode is activity in the electrochemical oxidation of a methanol at the electrochemical reduction and coincidence of oxygen.
[0016] On the other hand, it turns out that the direct mold methanol fuel cell by this invention is stable, without terminal voltage falling with time. Although this has produced the crossover of a methanol also in the fuel cell by this invention, and the carbon catalyst which supported the gold of a positive electrode is activity at the electrochemical reduction of oxygen, it is because it is inactive at the electrochemical oxidation of a methanol.
[0017]
[Effect of the Invention] As mentioned above, the direct mold methanol fuel cell concerning this invention is characterized by coming to have the positive electrode which has the catalyst which carries out electrochemical reduction of the oxygen selectively, and the negative electrode which has the catalyst which carries out electrochemical oxidation of the methanol. Lowering of the output by the crossover to the

positive electrode of the methanol of a negative electrode did not arise, but this configuration enabled it to obtain the high power stabilized for a long period of time.
[0018] Therefore, it is size at a contributing-on industry emergency.

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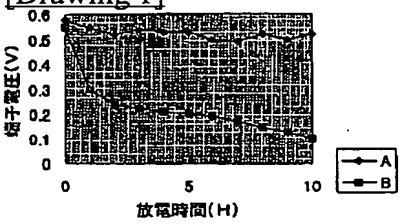
DRAWINGS

[Drawing 1]



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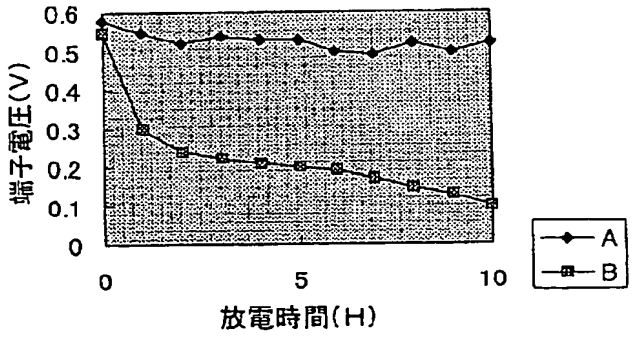
(54)【発明の名称】　直接型メタノール燃料電池

(57)【要約】
【課題】出力が高く、しかも長期間安定した出力を可能にする直接型メタノール燃料電池を提供する。
【解決手段】　本発明は、酸素を選択的に電気化学的還元する触媒を有する正極と、メタノールを電気化学的酸化する触媒を有する負極とを備えてなることを特徴とする。



【特許請求の範囲】

【請求項１】 酸素を選択的に電気化学的還元する触媒を有する正極と、メタノールを電気化学的酸化する触媒を有する負極とを備えてなることを特徴とする直接型メタノール燃料電池。

【請求項２】 正極の触媒が、金もしくは銀を担持したカーボン、金もしくは銀の少なくとも一方を有する合金を担持したカーボン又はこれら１種もしくは２種以上の混合物であることを特徴とする請求項１記載の直接型メタノール燃料電池。

【請求項３】 正極の触媒が、金粉体、銀粉体、カーボン粉体、金もしくは、銀の少なくとも一方を有する合金粉体又はこれら１種もしくは２種以上の混合物であることを特徴とする請求項１記載の直接型メタノール燃料電池。

【請求項４】 電解質が固体高分子膜であることを特徴とする請求項１、２又は３記載の直接型メタノール燃料電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、負極で燃料であるメタノールを直接かつ電気化学的に酸化する、直接型メタノール燃料電池に関するものである。

【０００２】

【従来の技術】現在、電気自動車に搭載されている燃料電池(FC)は、電解質に固体高分子膜を用いる固体高分子型燃料電池(PEFC)が主流であり、そのほとんどが、燃料に純水素を用いるものである。しかし、純水素は、ボンベや水素吸蔵合金により貯蔵されるが、車内の限られたスペースや重量制限を考えると実用化には問題がある。そこで、重量的、体積的にもｴﾈﾙｷﾞｰ密度が高く、取り扱いも容易なメタノールを燃料として用いることが注目されてきた。

【０００３】このメタノールを燃料として用いるには、メタノールを水素に改質してから燃料電池に送り込み電気化学的に反応させる間接型と、液体のメタノールをそのまま燃料電池に送り込み電気化学的に反応させる直接型とがある。直接型は、間接型に比べて装置が単純化できるため、電気自動車搭載用燃料電池として適している。

【０００４】直接型メタノール燃料電池は、正極と負極、およびそれらの間に挟まれる電解質からなる。電解質には、硫酸水溶液などの酸性電解液を用いるもの、水酸化カリウムなどのアルカリ性電解液を用いるもの、さらには固体高分子膜を用いたものがある。正極の触媒としては、Ptを担持したカーボン粉体が、負極の触媒としては Pt又はPt-Ruを担持したカーボン粉体が用いられている。

【０００５】直接型メタノール燃料電池では、正極で空気中の酸素還元が、負極で液体のメタノールの酸化が電気化学的に行われる。その反応式を下記に示す。

正極：$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

負極：$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

総反応：$CH_3OH + 3/2O_2 + H_2O \rightarrow CO_2 + 3H_2O$

【発明が解決しようとする課題】しかしながら、この直接型燃料電池は、電池の出力が低いという問題をかかえている。それは、負極のメタノールが電解質を通って対極である正極に移動する、いわゆるクロスオーバーに起因している。燃料であるメタノールのクロスオーバーは、本質的には一種の化学的短絡であり、正極で酸素の電気化学還元と同時にメタノールの電気化学的酸化が生じ、出力を著しく低下させる。これは、従来の直接型メタノール燃料電池の正極に用いられている触媒が、酸素の電気化学的還元と同時にメタノールの電気化学的酸化にも活性であるためである（M. P. Hogrth, ﾌﾟﾗﾁﾅ・ﾒﾀﾙｽﾞ・ﾚﾋﾞｭｰ, 40(4), 156, 1996）。しかし、具体的な構成についてはなにも言及されていない。

【０００６】

【課題を解決するための手段】そこで、本発明者は鋭意研究することにより、正極に酸素を選択的に電気化学的還元する触媒を、負極にメタノールを電気化学的酸化する触媒を有する負極を備えた直接型メタノール燃料電池とすることにより、クロスオーバーによる出力と効率の低下を防ぐことを可能にし、さらに金もしくは銀を担持したカーボン又は金もしくは銀の少なくとも一方を有する合金を担持したカーボン、又は金粉体、銀粉体、カーボン粉体もしくは金、銀の少なくとも一方を有する合金粉体、又はこれら１種もしくは２種以上の混合物が、酸素の電気化学的還元には活性であるのに対しメタノールの電気化学的酸化には不活性であるため、本発明の直接型燃料電池の正極の触媒として適することを見出した。

【０００７】

【発明の実施の形態】正極に酸素を選択的に電気化学的還元する触媒を、負極にメタノールを電気化学的酸化する触媒を備える直接型メタノール燃料電池とすることにより、負極の燃料であるメタノールが電解質を通って対極である正極に移動するクロスオーバーが生じても、正極の触媒がメタノールの電気化学的酸化には不活性であるため、酸素の電気化学的還元のみが行なわれ、メタノールの電気化学的酸化は行われない。そのため、クロスオーバーによる出力の低下が生じない。

【０００８】なお、本発明における「酸素を選択的に電気化学的還元する触媒」とは、次の１または２を意味する。１：酸素のみが電気化学的に還元される触媒。２：酸素の電気化学的還元と同時にメタノールの電気化学的酸化も生じるが、酸素の電気化学的還元量がメタノールの電気化学的酸化量に比べて極めて微量である触媒。

【０００９】また、本発明におけるカーボンとは、繊維状、球状、フレーク状等があげられ、粉体であってもよいし、焼結体等であってもよいし、これらに限られるも

のでもない。

【００１０】

【実施例】以下、本発明を好適な実施例により説明する。

【００１１】電解質として、固体高分子膜（デュポン社製、パーフルオロスルフォン酸膜・Nafion-117）を選択した。触媒電極ー接合体は、金を担持したカーボン触媒とPTFE粉体と固体高分子膜と同じ組成からなる溶液（アルドリッチ社製、Nafion溶液）との触媒混合物を塗布した多孔性カーボンペーパーを正極とし、また白金を担持したカーボン触媒とPTFE粉末との触媒混合物を塗布した多孔性カーボンペーパーを負極とし、固体高分子膜の両面ににホットプレスして作成した。ここで、カーボンにはアセチレンブラックを用いた。

【００１２】このようにして得られた触媒電極ー接合体を用いて燃料電池を組み、正極に空気を、負極にメタノールを送り、その経時特性を調べた。比較として、白金を担持したカーボン触媒とPTFE粉体と固体高分子膜と同じ組成からなる溶液との触媒混合物を塗布した多孔性カーボンペーパーを正極とした従来の燃料電池についても同じ条件で経時特性を調べた。

【００１３】図１において、Ａは本発明にかかる実施例の電池特性であり、Ｂは従来の電池特性である。

【００１４】ここで、試験条件を下記に示す。

【００１５】放電電流：２００ｍＡ／ｃｍ^2

正極供給：空気、５kg/cm^{2}Ｇ

負極：メタノール５０vol.%水溶液、常圧

作動温度：８０℃

図1より、従来型メタノール燃料電池の端子電圧は、負極のメタノールの正極へのクロスオーバーにより経時的に低下している。これは正極の白金を担持したカーボン触媒が、酸素の電気化学的還元と同時にメタノールの電気化学的酸化に活性であるためである。

【００１６】一方、本発明による直接型メタノール燃料電池は、経時的に端子電圧が低下することなく安定していることがわかる。これは、本発明による燃料電池においてもメタノールのクロスオーバーは生じているが、正極の金を担持したカーボン触媒が酸素の電気化学的還元には活性であるものの、メタノールの電気化学的酸化に不活性であるためである。

【００１７】

【発明の効果】以上、本発明にかかる直接型メタノール燃料電池は、酸素を選択的に電気化学的還元する触媒を有する正極と、メタノールを電気化学的酸化する触媒を有する負極を備えてなることを特徴とするものである。かかる構成により、負極のメタノールの正極へのクロスオーバによる出力の低下が生じず、長期間安定した高出力を得ることが可能となった。

【００１８】ゆえに、産業上に寄与すること非常に大である。

【図面の簡単な説明】

【図１】電解質に固体高分子膜を用いた、本発明の直接型燃料電池の経時特性図である。

【図１】